



Effects of bamboo cellulose nanowhisker content on the morphology, crystallization, mechanical, and thermal properties of PLA matrix biocomposites



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ABSTRACT

To improve the mechanical and thermal properties of poly (lactic acid) (PLA) composites, bamboo cellulose nanowhiskers (BCNW) were extracted and introduced into PLA composites as fillers. PLA/BCNW biofilms were fabricated by solution casting with different BCNW contents (0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 wt%). The characteristics of the biofilms were investigated by scanning electron microscopy (SEM), mechanical measurements, synchrotron radiation wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC). The results showed that the maximum tensile modulus and elongation at break of 427.72 ± 19.32 MPa and $22.27 \pm 3.50\%$ were reached at 2.5 wt% and 1.0 wt% loadings, respectively. Both homogeneity and stereocomplexed crystallites were observed, and heterogeneous nucleation effect was confirmed. With the addition of BCNW, the crystallite size of PLA/BCNW composites increased remarkably, and the largest crystallinity was $30.7 \pm 0.9\%$ with 2.5 wt% BCNW. These results provided data support for enlarging the application of PLA.

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1. Introduction

Poly(lactic acid) (PLA) is a green bioplastic that can be produced from natural sources such as corn and cassava. In addition, PLA degrades naturally into H₂O and CO₂ through composting [1–3]. With an ever-increasing public consciousness promoting environmental protection, the serious problem of “white pollution” is a cause for much concern; thus, PLA exhibits a wide degree of potential applications [4–6]. So far, the applications of PLA have involved biomedical devices, textiles, films, decorative panels, electrical components, food packages etc. [7–10]. However, the poor thermal stability and high brittleness of PLA leads to difficulties in processing and decreases the product's performance [3,11], limiting the wide application of PLA [12]. Thus, new effective methods to improve the thermal and mechanical properties of PLA are of great interest.

The employment of bio-nanoparticles as reinforcements in PLA

composites has been proved to be a valid method [2]. Recent studies reported that cellulose nanowhiskers (CNW), with a large aspect ratio, high strength, and elastic modulus reinforced PLA composites and presented excellent thermal and mechanical properties [13–18]. Moso bamboo (*Phyllostachys heterocycla*) grows abundantly in many tropical and subtropical regions of the world, especially in Zhejiang Province, China. It has been widely used in furniture manufacturing, construction materials and household items due to the advantages of fast growth, high strength, surface hardness and easy machinability [19–22]. However, a large amount of moso bamboo processing residue is underused. The cellulose content of bamboo is 40%–65%, which is comparable to wood [23]. Thus, bamboo residue is a good resource for renewable nano-biobased filler. Brito et al. [24] and Lu et al. [25] prepared cellulose nanocrystals with a length of approximately 100 nm by the hydrolysis of bamboo fibers in the presence of sulfuric acid and phosphoric acid. Visakh et al. [26] employed bamboo cellulose nanowhiskers (BCNW) as reinforcements in rubber composites and found that the BCNW with high length and aspect ratios improved the performance of composites. Our group prepared bamboo cellulose nanowhisker from bamboo residues, and investigated the mechanism of acid hydrolysis [27]. BCNW may act as a nucleating

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agent or plasticizer, and has been used as an applicable nanofiller in PLA composites [28,29]. In this regard, the crystallization performance, thermal property, and mechanical properties of the composites would be improved. Lee et al. [30] found that all properties of thermology, rheology and mechanics increased with the addition of CNW (0.1 wt% and 0.5 wt%) into PLA composites. Additionally, acetylated-CNW with different contents (1 wt%, 2 wt%, 3 wt%) reinforced PLA composites were also reported; the crystallization behavior and mechanical properties of the composites were improved. These composites can be used in artificial bone and biomembranes, etc. [31]. Arias et al. [32] prepared PEO-coated nanocrystals, with the cellulose nanocrystals (CNC) evenly dispersed in the PLA matrix, and studied the performance of composites with different CNC contents. Arjmandi et al. [28] investigated the reinforcement mechanism of a montmorillonite/CNW/PLA ternary system and found that the three compositions with proportions of 5:1:10 presented the highest tensile properties. Sanchez-Garcia et al. [33] concluded that PLA/CNW composites had better mechanical properties with a CNW loading below 3 wt%.

Although it was previously reported that the thermal and mechanical properties of a PLA composite would be enhanced to some extent by adding CNW, the agglomeration of CNW would decrease the thermal and mechanical properties of PLA in some cases due to the abundant hydroxyl groups [34–36]. Thus, the optimal content of CNW incorporated into a PLA matrix remains to be explored. In addition, the unique morphology of BCNW and the effects of different BCNW contents on the crystallization behavior and macroscopic property of PLA biocomposites still needs to be further investigated.

In this paper, BCNW were extracted from bamboo residue through hydrolysis in the presence of sulfuric acid. The morphology of the BCNW was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Nanocomposite films were prepared through incorporating different contents of BCNW into a PLA matrix using a solution casting method. The reinforcement mechanism of BCNW in the PLA composites was studied. The interface characteristics of the composites were observed by SEM. The crystallite structures of the composites were investigated by synchrotron radiation wide angle X-ray scattering (WAXS). The crystallization behavior and thermal performance were characterized by differential scanning calorimetry (DSC). The tensile strength, tensile modulus, and elongation at break of the composites were investigated. On the basis of these results, the optimal BCNW content in a PLA matrix was obtained. These results provided basic reference data for further improving the properties of PLA biocomposites and achieving extensive applications in engineering fields.

2. Materials and methods

2.1. Materials

Moso bamboo residues were kindly supplied by a local moso bamboo processing factory, Lin'an, Zhejiang Province, China. The particles were screened through a mesh size of 100 and dried at 105 °C to constant quality for further use. PLA (4032D) was produced by the NatureWorks Corporation (USA). The density was 1.25 g/cm³, and the molecular weight was 52,000 g/mol. All other reagents and solvents were used as received from the commercial source.

2.2. Preparation and characterization of bamboo cellulose nanowhiskers (BCNW)

Bamboo particles (BP) (<150 μm) were mercerized with a NaOH solution followed by bleaching with a NaClO₂ solution before

hydrolyzing. Then, the bleached cellulose was hydrolyzed in a 65 wt% sulfuric acid solution at 45 °C for 3 h. The procedure was in accordance with previous work [27]. Nevertheless, different acid solution concentrations and hydrolysis times were tried and it was observed that lower concentration led to insufficient hydrolysis, but higher treatment times led to carbonization and darkening of the product.

BCNW was checked for micromorphology by transmission electron microscopy (TEM) using a JEM 1230 (JEOL, Japan) equipped with a digital Image Tools software (UTHSCSA, USA). A BCNW aqueous suspension of 0.05 wt% was ultrasonically treated for 30 min. Samples were then stained in a 2 wt% solution of uranyl acetate for 3 min. Drops of the stained samples were deposited on copper TEM grids, and the excess water was absorbed with a tissue. The surface morphology of the raw bamboo particles and BCNW were observed using a field launch scanning electron microscope (S-8010, Hitachi, Japan). All samples were coated with gold before observation. The launching voltage of the electron microscope was 4.0 kV.

2.3. Fabrication and observation of PLA/BCNW composites film

Approximately 5.0 g PLA was added to 60 mL chloroform and stirred in a 50 °C water bath until PLA dissolved completely. The solution was blended with different contents of dried BCNW, and ultrasonic stirring was used for 30 min to disperse the solution. The blended solution was cast in a self-made PTFE mold (diameter of 80 mm) and dried at room temperature for 48 h. This resulted in PLA/BCNW biocomposite films with a thickness of 0.3–0.5 mm. The surface morphology of composites with different BCNW contents was also observed using a scanning electron microscope (S-8010, Hitachi, Japan).

2.4. Tensile test

Tensile tests of PLA/BCNW composites were performed on a universal testing machine at room temperature (CMT4503, MTS, Inc.). A self-made knife was used to cut the films into dumbbell shaped specimens with a length of 50 mm, a cross-sectional width of 4.0 mm and an initial gauge length of 15 mm [37]. A fixed crosshead rate for tension of 20 mm/min was utilized in all cases and the results were calculated based on the average results from five specimens.

2.5. Differential scanning calorimetry (DSC)

DSC (200F3, Netzsch) was adopted to study the thermal properties of pure PLA and the biocomposites. Approximately 10.0 mg sample were weighed and hermetically sealed. The samples were heated from room temperature to 180 °C at a rate of 10 °C/min, maintained for 3 min, cooled to 0 °C at a rate of 10 °C/min and heated again to 180 °C at a rate of 10 °C/min. The second DSC thermograms were recorded for further evaluation. Nitrogen was used as a purging gas at a rate of 50 mL/min. An empty aluminum pan was used as a reference. Thermal property parameters were calculated based on the average of three specimens. Cold crystallization degree (X_{cc}) was estimated according to the following equation,

$$X_{cc}(\%) = \frac{\Delta H_{cc}}{\Delta H_0 \times X_{PLA}} \times 100\% \quad (1)$$

where, ΔH_{cc} refers to the cold crystallization enthalpy of PLA/BCNW composites; ΔH_0 refers to the enthalpy value during 100% crystallization of PLA, which is 93.6 J/g [38]; and X_{PLA} refers to the weight

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